The Interaction of Group 15 And 16 Donor Ligands with the Later Transition Metals

A Collection of Published Papers Presented in Application for the Degree of Doctor of Science at Massey University

Andrew M. Brodie BSc(Hons) PhD FNZIC CChem FRSC

1999

ACKNOWLEDGEMENTS

One of the most enjoyable aspects of research, apart from the excitement of seeing beautiful crystals of a new compound coming out of solution, is the chance to collaborate with a number of talented and like-minded people. This is certainly the case for me and I would particularly like to thank Associate Professor Eric W. Ainscough for his long and fruitful collaboration on virtually all of the papers included in this thesis. Our research programme has been a partnership which I have valued tremendously.

Other collaborators have brought their knowledge and skills to the publications and they are listed as co-authors. It should be noted that many of these researchers were outstanding graduate students gaining training in research as part of their BSc(Hons), MSc or PhD degree programmes. The input of these people has added a richness to our research and they are gratefully thanked. Special mention must be made of the X-ray crystallographers, Dr Kevin Brown, Professor Ted Baker, Dr Graeme Gainsford, Associate Professor Joyce Waters and, most recently, Professor Tony Burrell, who determined the structures described in the papers. X-ray crystallography has certainly developed tremendously over the last 30 years and it is inconceivable that the modern synthetic inorganic chemist could be without access to this vital technique.

We have also had a valuable collaboration with Professor Ted Baker and his coworkers in the metalloprotein area and their contribution to the papers in which protein structures are described is obviously substantial.

I thank all of the past and present staff (technical, secretarial and academic) in Chemistry for making this an enjoyable and stimulating place in which to work.

Finally, I acknowledge the many years of loving support received from my family, especially Carolyn.

CONTENTS

INTRODUCTION

The scientific publications contained in this thesis* are the results of approximately 30 years of transition metal chemistry research, mainly pursued at Massey University. The emphasis has been on the synthesis of interesting new compounds and their subsequent characterisation using a variety of physicochemical techniques. Where appropriate reactivity studies have also been carried out on the new compounds.

Chapter 1 contains papers concerned with ligands containing the Group 16 donor, sulfur, although there are a few selenium donors included. The particular ligands studied are tertiary phosphine and arsine chalcogenides, thioamides, thioureas, thiolates and thioethers with copper and the carbonyls of Group 6 and osmium.

In Chapter 2, papers detailing research into the metal binding properties of the human milk protein, lactoferrin and related small molecule systems containing phenolate donors are grouped together. A number of relevant copper thiolate systems are included in this chapter as well, which link to the paper on the blue copper protein, azurin. Finally, in this chapter, are papers describing the preparation and characterisation of a number of complexes related to the antitumour copper(II) 2-formylpyridine thiosemicarbazone system.

The theme for Chapter 3 is Group 15 donor ligand complexes, in particular those of nitrogen and phosphorus. The discovery that *N*-phenylthiourea could be desulfurized in a reaction with copper(II) led to the investigation of phenylcyanamides as ligands. A number of tertiary phosphine ligands have been examined, including the bulky tribenzylphosphine, and research in this area is continuing.

Papers with an organometallic theme form the contents of Chapter 4.

---

* Papers accepted for publication are not included but are listed in each chapter for completeness.

CHAPTER 1

SULFUR DONOR LIGAND COMPOUNDS

CHAPTER 1

1. Tertiary phosphine and arsine chalcogenide derivatives of the Group VI metal carbonyls. Ainscough, E. W.; Brodie, A. M.; Furness, A. R. *J. Chem. Soc., Chem. Commun.* (1971) 1357.

2. Synthesis and reactivity of Group VA chalcogenide 1,5-cyclooctadiene rhodium(I) and iridium(I) complexes. Ainscough, E. W.; Brodie, A. M.; Mentzer, E. *J. Chem. Soc., Dalton Trans.* (1973) 2167-71.

3. Tertiary phosphine and arsine chalcogenide derivatives of Group VI metal carbonyl complexes. Ainscough, E. W.; Brodie, A. M.; Furness, A. R. *J. Chem. Soc., Dalton Trans.* (1973) 2360-3.

4. Interaction of dimethyl(dimethylarsinothio)arsine sulfide with Group 6 metal carbonyls. Ainscough, E. W.; Brodie, A. M.; Leng-Ward, G. *J. Chem. Soc., Dalton Trans.* (1974) 2437-8.

5. Infrared, Raman and NQR studies of some trimethylphosphine sulfide and trimethylarsine sulfide copper(I) complexes. Bowmaker, G. A.; Whiting, R.; Ainscough, E. W.; Brodie, A. M. *Aust. J. Chem.* (1975) 28, 1431-8.

6. Bidentate tertiary phosphine sulfide complexes of copper and a crystal structure of a three coordinate copper(I) complex. Ainscough, E. W.; Bergen, H. A.; Brodie, A. M.; Brown, K. L. *J. Inorg. Nucl. Chem.* (1976) 38, 337-8.

7. Sulfur-ligand-metal complexes. Part 4. Copper complexes with bidentate tertiary-phosphate sulfide and selenide ligands and the crystal structure of a three-coordinate copper(I) complex. Ainscough, E. W.; Bergen, H. A.; Brodie, A. M.; Brown, K. A. *J. Chem. Soc., Dalton Trans.* (1976) 1649-56.

8. Sulfur ligand metal complexes. Part 5. Disecondary sulfide and related ligand complexes of the Group VI metal carbonyls. Ainscough, E. W.; Birch, E. J; Brodie, A. M. *Inorg. Chim. Acta* (1976) 20, 187-92.

9. Sulfur ligand metal complexes. Part 6. Copper complexes of 2,5-dithiahexane and 3,6-dithiaoctane. Ainscough, E. W.; Brodie, A. M.; Palmer, K. C. *J. Chem. Soc., Dalton Trans.* (1976) 2375-81.

10. Sulfur-ligand-metal complexes. Part 7. The interaction of some diphosphine dichalcogenides and tetra-alkylthiuram disulfides with halogens and some first-row transition-metal salts. Ainscough, E. W.; Brodie, A. M.. *J. Chem. Soc., Dalton Trans.* (1977) 565-70.

11. Sulfur-ligand-metal complexes. Part 8. Bis(diphenylphosphino-thioyl)methane complexes of copper(I). Ainscough, E. W.; Brodie, A. M.; Brown, K. L. *J. Chem. Soc., Dalton Trans.* (1980) 1042-7.

12. Sulfur ligand metal complexes. Part 9. Aryl sulfide complexes of the Group VI metal carbonyls. Ainscough, E. W.; Brodie, A. M.; Larsen, N. G.; Mathews, R. G. *Inorg. Chim. Acta* (1981) 49, 159-66.

13. Sulfur ligand metal complexes. Part 10. Sulfur-nitrogen donor ligand complexes of the Group VI metal carbonyls. Ainscough, E. W.; Brodie, A. M.; Larsen, N. G.; Stevens, M. R. *Inorg. Chim. Acta* (1981) 50, 215-20.

14. Copper coordination to thioether ligands. Chemical, spectroscopic, and crystallographic studies on copper(I) complexes of 2-(3,3-dimethyl-2-thiobutyl)pyridine and the 2-(3,3-dimethyl-2-thiobutyl)pyridinium cation. Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Larsen, N. G.; Brown, K. L. *J. Chem. Soc., Dalton Trans.* (1981) 1746-52.

15. Copper coordination to thioether ligands. Spectroscopic studies of dimeric copper(II) complexes of 2-(3,3-dimethyl-2-thiabutyl)pyridine and the crystal structure of di-μ-bromobis{bromo[2-(3,3-dimethyl-2-thiabutyl)pyridine-N,S]copper(II)}. Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Larsen, N. G. *J. Chem. Soc., Dalton Trans.* (1981) 2054-8.

16. Sulfur ligand metal complexes. Part 13. Palladium(II) and platinum(II) complexes of pentafluoroaryl thioether ligands. Ainscough, E. W.; Brodie, A. M.; Larsen, N. G.; Gin, A.; Weiner, M. A. *Inorg. Chim. Acta* (1981) 53, L271-L273.

17. Sulfur-ligand-metal complexes. Part 14. Bis[2(3,3-dimethyl-2-thiabutyl)pyridine] complexes of copper(II) and related metal ions. Ainscough, E. W.; Brodie, A. M.; Larsen, N. G. *J. Chem. Soc., Dalton Trans.* (1982) 815-19.

18. Sulfur ligand metal complexes. Part 15. Sulfur-nitrogen donor ligand complexes of copper. Ainscough, E. W.; Brodie, A. M.; Larsen, N. G. *Inorg. Chim. Acta* (1982) 60, 25-34.

19. The interaction of heterocyclic thioamides with triosmium clusters: the X-ray crystal structure of (μ-H)$Os_3(CO)_{10}$(μ-SC:NCH_2CH_2S). Brodie, A. M.; Holden, H. Diane; Lewis, J.; Taylor, M. J. *J. Organomet. Chem.* (1983) 253, C1-C4.

20. Sulfur ligand-metal complexes. Part 16. Copper complexes of thio ethers and the single-crystal X-ray structure of the polymeric mixed-valence complex, penta-μ-chloro-tris-μ-tetrahydrothiophenetetra-copper(I,II). Ainscough, E. W.; Brodie, A. M.; Husbands, J. M.; Gainsford, G. J.; Gabe, E. J.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* (1985) 151-8.

21. The production of the sulfate anion by interaction of thioamides with copper compounds in pyridine solvent. Ainscough, E. W.; Bingham, A. G.; Brodie, A. M. *Inorg. Chim. Acta* (1985) 96, L47-L48.

22. Copper promoted reactions of the heterocyclic thioamide, 2-thiazolidinethione. Ainscough, E. W.; Anderson, B. F.; Baker, E. N.; Bingham, A. G.; Brader, M. L.; Brodie, A. M.; Gainsford, G. J. *Inorg. Chim. Acta* (1985) 105, L5-L7.

23. The reaction of bis(acetonitrile)decacarbonyltriosmium with heterocyclic thioamides. The crystal and molecular structure of 1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-μ-hydrido-1,2-μ-(thiazoline-2-thiolato)-triangulo-triosmium. Brodie, A. M.; Holden, H. D.; Lewis, J.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* (1986) 633-9.

24. The interaction of 1-methylimidazoline-2(3*H*)-thione with copper(II) salts. Ainscough, E. W.; Baker, E. N.; Bingham, A. G.; Brodie, A. M. *J. Chem. Soc., Dalton Trans.* (1989) 39-42.

25. Interaction of benzo-1,3-thiazoline-2-thione and related ligands with copper(II) salts and the single-crystal x-ray structure of μ-[1,2-bis(diphenylphosphino)ethane]-bis{(benzo-1,3-thiazole-2-thiolato-*S*)[1,2-bis(diphenylphosphinoethane]copper(I)}. Ainscough, E. W.; Baker, E. N.; Bingham, A. G.; Brodie, A. M.; Smith, C. A. *J. Chem. Soc., Dalton Trans.* (1989) 2167-71.

26. Copper(II)-promoted oxidation of mercaptocarboxylic acids. The characterization of disulfide- and oxalate-containing products. Crystal structures of [{Cu(bipy)(2,2'-dtdp)}$_n$].3nH$_2$O and [{Cu(bipy)(3,3'-dtdp)}$_n$].2nH$_2$O (bipy = 2,2'-bipyridine, dtdp = dithiodipropanoate). Brader, M. L.; Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Lewandoski, D. A. *J. Chem. Soc., Dalton Trans.* (1990) 2089-94.

27. The copper promoted oxidation of 1-methylimidazoline-2(3*H*)-thione to bis(1-methylimidazol-2-yl)sulfide. Ainscough, E. W.; Brader, M. L.; Brodie, A. M.; Gainsford, G. J. *Inorg. Chim. Acta* (1991) 180, 81-3.

28. The synthesis and single-crystal X-ray structure of [{$Os_3H(CO)_{10}$}$_3$($S_3C_3N_3$)]; a novel osmium cluster containing three linked osmium triangles. Ainscough, E. W.; Brodie, A. M.; Coll, R. K.; Mair, A. J. A.; Waters, J. M. *Inorg. Chim. Acta* (1993) 214, 21-2.

29. Synthesis and photochemical reactivity of phenylthioureatotriosmium cluster complexes: crystal structures of [$Os_3H(CO)_{10}${μ-SC(NPh)(NHPh)}] and [$Os_3H(CO)_9${μ_3-SC(NPh)(NHPh)}]. Ainscough, E. W.; Brodie, A. M.; Ingham, S. L.; Kotch, T. G.; Lees, A. J.; Lewis, J.; Waters, J. M. *J. Chem. Soc., Dalton Trans.* (1994) 1-6.

30. Linked triosmium cluster complexes containing thiolato-carboxylato ligands: the crystal and molecular structures of [{$Os_3H(CO)_{10}$}$_2$(μ-$SC_6H_4CO_2$)] and [{$Os_3H(CO)_{10}$}$_2$(μ-2)]. Ainscough, E. W.; Brodie, A. M.; Coll, R. K.; Mair, A. J. A.; Waters, J. M. *J. Organomet. Chem.* (1996) 509, 259-64.

31. The photochemical reactivity of triosmium cluster complexes containing 2-mercaptopyridine ligands: the crystal and molecular structures of the linked clusters [{$Os_3H(CO)_{10}$}$_2$(μ-$SC_5H_3NCO_2$)] and [{$Os_3H(CO)_9$}(μ-$SC_5H_3NCO_2$)-{$Os_3H(CO)_{10}$}]. Ainscough, E. W.; Brodie, A. M.; Coll, R. K.; Kotch, T. G.; Lees, A. J.; Mair, A. J. A.; Waters, J. M. *J. Organomet. Chem.* (1996) 517, 173-181.

32. The reaction of [$Os_3(CO)_{10}(CH_3CN)_2$] with carboxylic acids: the crystal and molecular structures of [$Os_3H(CO)_{10}(C_6H_4(OH)CO_2)$] and [$Os_3H(CO)_{10}(C_6H_5COS)$]. Ainscough, E. W.; Brodie, A. M.; Coll, R. K.; Coombridge, B. A.; Waters, J. M. *J. Organomet. Chem.* (1998) 556, 197-205.

33. The interaction of triosmium clusters with pyridine thiols: the crystal and molecular structures of [{Os_3(μ-H)$(CO)_{10}$}$_2$(μ-$S_2C_4H_2N_2$)] and [Os_3(μ-H)$(CO)_{10}$(μ-SC_5H_4N)]. Ainscough, E. W.; Brodie, A. M.; Coll, R. K.; Waters, J. M. *Aust. J. Chem.* (1999) 52, 801-805.

CHAPTER 2

BIOINORGANIC AND RELATED SYSTEMS

CHAPTER 2

1. The chromium, manganese, cobalt and copper complexes of human lactoferrin. Ainscough, E. W.; Brodie, A. M.; Plowman, J. E. *Inorg. Chim. Acta* (1979) 33, 149-53.

2. The interaction of ethylenediamine-*N,N'*-di(*o*-hydroxyphenylacetic acid) with metal ions in ethanol. Ainscough, E. W.; Brodie, A. M.; Plowman, J. E. *J. Inorg. Nucl. Chem.* (1979) 41, 1257-60.

3. Zinc transport by lactoferrin in human milk. Ainscough, E. W.; Brodie, A. M.; Plowman, J. E. *Am. J. Clin. Nutr.* (1980) 33, 1314-15.

4. Studies on human lactoferrin by electron paramagnetic resonance, fluorescence, and resonance Raman spectroscopy. Ainscough, E. W.; Brodie, A. M.; Plowman, J. E.; Bloor, S. J.; Loehr, J. S.; Loehr, T. M. *Biochemistry* (1980) 19, 4072-9.

5. Small molecule analogs for the specific iron-binding site of lactoferrin: a single-crystal X-ray structure of bis(methanol)bis[2-(5-methylpyrazol-3-yl)phenolato]-iron(III) nitrate-methanol and spectroscopic studies on iron(III) phenolate complexes. Ainscough, E. W.; Brodie, A. M.; Plowman, J. E.; Brown, K. L.; Addison, A. W.; Gainsford, A. R. *Inorg. Chem.* (1980) 19, 3655-63.

6. Small molecule analogs for the specific metal-binding site of lactoferrin. Part 2. Phenolato complexes of copper(II) and the nature of the charge-transfer transition in the visible region. Ainscough, E. W.; Bingham, A. G.; Brodie, A. M.; Husbands, J. M.; Plowman, J. E. *J. Chem. Soc., Dalton Trans.* (1981), 1701-7.

7. Spectroscopic studies on copper(II) complexes of human lactoferrin. Ainscough, E. W.; Brodie, A. M.; McLachlan, S. J.; Ritchie, V. S. *J. Inorg. Biochem.* (1983) 18, 103-12.

8. The reaction of 1,1'-biphenyl-2,2'-diol with iron(III) and the crystal structure of piperidinium bis[μ-(1,1'-biphenyl-2,2'-diolato-*O*,μ-*O'*)(1,1'-biphenyl-2,2'-diolato-*O*,*O'*)ferrate(III)]-ethanol(1/2). Ainscough, E. W.; Brodie, A. M.; McLachlan, S. J.; Brown, K. L. *J. Chem. Soc., Dalton Trans.* (1983), 1385-9.

9. Synthetic, spectroscopic, and X-ray crystallographic studies on binuclear copper(II) complexes with a tridentate NNS-bonding 2-formylpyridine thiosemicarbazone ligand. The characterization of both neutral and deprotonated coordinated ligand structures. Bingham, A. G.; Boegge, H.; Mueller, A.; Ainscough, E. W.; Brodie, A. M. *J. Chem. Soc., Dalton Trans.* (1987) 493-9.

10. Spectrochemical studies on the blue copper protein azurin from Alcaligenes denitrificans. Ainscough, E. W.; Bingham, A. G.; Brodie, A. M.; Ellis, W. R.; Gray, H. B.; Loehr, T. M.; Plowman, J. E.; Norris, G. E.; Baker, E. N. *Biochemistry* (1987) 26, 71-82.

11. The interaction of thiols with copper(II): an electron spin resonance study. Ainscough, E. W.; Bingham, A. G.; Brodie, A. M. *Inorg. Chim. Acta* (1987) 138, 175-7.

12. The synthesis and characterization of new phenolato complexes of copper(II) and some adducts with ethylenediamine. Ainscough, E. W.; Bingham, A. G.; Brodie, A. M.; Englebretsen, D. R.; Husbands, J. M. *J. Chem. Res., (S)* (1988) 60-1; *(M)* 1988, 0519.

13. The characterization of both the coordinated and noncoordinated saccharinate ion. The syntheses and crystal structures of aqua(2-formylpyridine thiosemicarbazonato)-(saccharinato-*N*)copper(II) hemihydrate and 2,2'-bipyridyl-(2-formylpyridine thiosemicarbazonato)copper(II) saccharinate dihydrate. Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Cresswell, R. J.; Ranford, J. D.; Waters, J. M. *Inorg. Chim. Acta* (1990) 172, 185-90.

14. Reaction of nitrogen and sulfur donor ligands with the antitumor copper complex $[\{CuL(MeCO_2)\}_2]$ (HL = 2-formylpyridine thiosemicarbazone) and the single-crystal X-ray structure of 2,2'-bipyridine-κ^2N,N')(2-formylpyridine-κN thiosemicarbazonato-κ^2N^1,S)copper(II) perchlorate. Ainscough, E. W.; Brodie, A. M.; Ranford, J. D.; Waters, J. M. *J. Chem. Soc., Dalton Trans.* (1991) 1737-42.

15. Preparation and characterization of complexes of the antitumor copper(II) 2-formylpyridine thiosemicarbazone (HL) system and the single-crystal X-ray structures of $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ and $[Cu(HL)(H_2O)(ClO_4)_2].2H_2O$. Ainscough, E. W.; Brodie, A. M.; Ranford, J. D.; Waters, J. M. *J. Chem. Soc., Dalton Trans.* (1991) 2125-31.

16. Anion binding by human lactoferrin: results from crystallographic and physicochemical studies. Shongwe, M. S.; Smith, C. A.; Ainscough, E. W.; Baker, H. M.; Brodie, A. M.; Baker, E. N. *Biochemistry* (1992) 31, 4451-8.

17. The reaction of the pyrophosphate ion with the antitumor complex $[\{CuL(CH_3COO)\}_2]$ (HL = 2-formylpyridine thiosemicarbazone) and the single-crystal X-ray structure of $[(CuL)_4P_2O_7]\cdot nH_2O$. Ainscough, E. W.; Brodie, A. M.; Ranford, J. D.; Waters, J. M.; Murray, K. S. *Inorg. Chim. Acta* (1992) 197, 107-15.

18. The effect of strong NH···S hydrogen bonds in the copper(I) thiolate complex, $(NEt_4)_2[Cu(o\text{-pabt})_3]$ (*o*-pabt = *o*-pivaloylamino-benzenethiolato). Okamura, T.; Ueyama, N.; Nakamura, A.; Ainscough, E. W.; Brodie, A. M.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* (1993) 1658-60.

19. Molecular structure of $[Mn^{III}L_2]^-$ [H_2L = N-(3,5-dichloro-2-hydroxybenzyl)glycine]: evidence for a pseudo-Jahn-Teller compression. Shongwe, M. S.; Mikuriya, M.; Ainscough, E. W.; Brodie, A. M. *J. Chem. Soc., Chem. Commun.* (1994) 887-8.

20. Specific binding of cerium by human lactoferrin stimulates the oxidation of Ce^{3+} to Ce^{4+}. Smith, C. A.; Ainscough, E. W.; Baker, H. M.; Brodie, A. M.; Baker, E. N. *J. Am. Chem. Soc.* (1994) 116, 7889-90.

21. Complexes of human lactoferrin with vanadium in oxidation states +3, +4 and +5. Smith, C. A.; Ainscough, E. W.; Brodie, A. M. *J. Chem. Soc., Dalton Trans.* (1995) 1121-6.

22. Hexafluorosilicate coordination to the antitumor copper(II) salicylaldehyde benzoylhydrazone (H_2L) system: single-crystal X-ray structure of $[\{Cu(HL)H_2O\}_2SiF_6]\cdot 2H_2O$. Ainscough, E. W.; Brodie, A. M.; Ranford, J. D.; Waters, J. M. *Inorg. Chim. Acta* (1995) 236, 83-8.

23. The examination of preservative-treated radiata pine using elctron spin resonance spectroscopy. Plackett, D. V.; Ainscough, E. W.; Brodie, A. M. *Wood Protection* (1995) 3, 41-46.

24. Anion binding by transferrins: importance of second-shell effects revealed by the crystal structure of oxalate-substituted diferric lLactoferrin. Baker, H. M.; Anderson, B. F.; Brodie, A. M.; Shongwe, M. S.; Smith, C. A.; Baker, E. N. *Biochemistry* (1996) 35, 9007-9013.

25. Reaction of anionic oxygen donors with the antitumor copper(II)-pyridine-2-carbaldehyde thiosemicarbazone (HL) system and the crystal structure of $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2{\cdot}2H_3PO_4{\cdot}2H_2O$. Ainscough, E. W.; Brodie, A. M.; Ranford, J. D.; Waters, J. M. *J. Chem. Soc., Dalton Trans.* (1997) 1251-1255.

26. Antitumor copper(II) salicylaldehyde benzoylhydrazone (H_2sb) complexes: physicochemical properties and the single-crystal X-ray structures of $[\{Cu(H_2sb)(CCl_3CO_2)_2\}_2]$ and $[\{Cu(Hsb)(ClO_4)(C_2H_5OH)\}_2]$ and the related salicylaldehyde acetylhydrazone (H_2sa) complex, $[Cu(Hsa)Cl(H_2O)]{\cdot}H_2O$. Ainscough, E. W.; Brodie, A. M.; Dobbs, A. J.; Ranford, J. D.; Waters, J. M. *Inorg. Chim. Acta* (1998) 267, 27-38.

27. Synthetic, spectroscopic, and x-ray crystallographic studies on the uranyl(VI) complexes of the β-diketophenol ligands 1-(2-hydroxyphenyl)-1,3-butanedione and 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione. Ainscough, E. W.; Brodie, A. M.; Cresswell, R. J.; Waters, J. M. *Inorg. Chim. Acta* (1998) 277, 37-45.

28. Nitrogen, sulfur and oxygen donor adducts with copper(II) complexes of antitumor 2-formylpyridinethiosemicarbazone analogs: physicochemical and cytotoxic studies. Ainscough, E. W.; Brodie, A. M.; Denny, W. A.; Finlay, G. J.; Ranford, J. D. *J. Inorg. Biochem.* (1998) 70, 175-185.

29. A series of heteroleptic complexes of the type fac-$[Mn^{III}L_2]^-$ [H_2L = derivatives of *N*-(2-hydroxybenzyl)glycine or *N*-(5-nitro-2-hydroxybenzyl)sarcosine] possessing unusual Mn(III) co-ordination spheres. Shongwe, M. S.; Mikuriya, M.; Nukada, R.; Ainscough, E. W.; Brodie, A. M.; Waters, J. M. *Inorg. Chim. Acta* (1999) 290, 228-236.

30. Cytotoxity of salicylaldehyde benzoylhydrazone analogues and their transition metal complexes: quantitative activity relationships. Ainscough, E. W.; Brodie, A. M.; Denny, W. A.; Finlay, G. J.; Gothe, S. A.; Ranford, J. D. *J. Inorg. Biochem.* (1999) in the press.

CHAPTER 3

NITROGEN AND PHOSPHORUS DONOR LIGAND COMPOUNDS

CHAPTER 3

1. Metal complexes of phosphorus-nitrogen ligands. Part 1. Synthesis and reactivity of some phosphinoaminopyridine complexes of Group 6 metal carbonyls and of bromopentacarbonylmanganese(I). Ainscough, E. W.; Brodie, A. M.; Wong, S. T. *J. Chem. Soc., Dalton Trans.* (1977) 915-20.

2. Copper and related metal complexes with *NN'*-(1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-diylidene)dianiline ligands. Brodie, A. M.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* (1979) 199-204.

3. The crystal structure of chlorotris(3-methylpyridine)copper(I), and its conversion into hexa-μ-chlorotetrakis(3-methylpyridine)-μ_4-oxotetracopper(II). Ainscough, E. W.; Bingham, A. G.; Brodie, A. M.; Brown, K. L. *J. Chem. Soc., Dalton Trans.* (1984) 989-91.

4. Copper(II) promoted desulfurization of *N*-phenylthiourea. The synthesis and X-ray structure of [{Cu(bipy)(pc)2}2] (bipy = 2,2'-bipyridine, pc = phenylcyanamide). Brader, M. L.; Ainscough, E. W.; Baker, E. N.; Brodie, A. M.. *Polyhedron* (1989) 8, 2219-21.

5. Synthetic, spectroscopic, and X-ray crystallographic studies on phenylcyanamido-copper(II) complexes. the characterization of three different coordination modes for phenylcyanamide anions. Brader, M. L.; Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Ingham, S. L. *J. Chem. Soc., Dalton Trans.* (1990) 2785-92.

6. Synthetic, spectroscopic and X-ray crystallographic studies on phenylcyanamido-copper(I) complexes. Ainscough, E. W.; Baker, E. N.; Brader, M. L.; Brodie, A. M.; Ingham, S. L.; Waters, J. M.; Hanna, J. V.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* (1991) 1243-9.

7. Synthesis and structural characterization of five-coordinate copper(I) and silver(I) 2,2':6',2"-terpyridine complexes. Ainscough, E. W.; Brodie, A. M.; Ingham, S. L.; Waters, J. M. *J. Chem. Soc., Dalton Trans.* (1994) 215-20.

8. Functionalized phosphines: structure of bis[(2-aminophenyl)diphenylphosphine-κ^2N,P]copper(I) perchlorate ethanol solvate. Ainscough, E. W.; Brodie, A. M.; Ingham, S. L.; Waters, J. M. *Inorg. Chim. Acta* (1994) 217, 191-4.

9. Reactivity of triosmium clusters with substituted triphenylphosphines: the crystal and molecular structure of $[HOs_3(CO)_9(2\text{-}PNH)]$ ($2\text{-}PNH_2$ = 2-aminophenyldiphenyl-phosphine). Ainscough, E. W.; Brodie, A. M.; Ingham, S. L.; Waters, J. M. *J. Organomet. Chem.* (1994) 468, 229-34.

10. Functionalized phosphine complexes of Group 6 metal carbonyls: structure of pentacarbonyl(phenyl-2-carbaldehyde diphenylphosphine-κP)tungsten. Ainscough, E. W.; Brodie, A. M.; Ingham, S. L.; Waters, J. M. *Inorg. Chim. Acta* (1995) 234, 163-7.

11. Synthesis and structural characterization of a pair of linkage isomers of copper(I) pyridine-2-carbaldehyde 2'-pyridylhydrazone complexes. Ainscough, E. W.; Brodie, A. M.; Ingham, S. L.; Waters, J. M. *Inorg. Chim. Acta* (1996) 249, 47-55.

12. Anisotropy in the ^{31}P, $^{63/65}Cu$ indirect spin-spin coupling and ^{31}P nuclear shielding tensors of linear copper(I) phosphines. Kroeker, S.; Hanna, J. V.; Wasylishen, R. E.; Ainscough, E. W.; Brodie, A. M. *J. Magn. Reson.* (1998) 135, 208-215.

13. Two-Coordinate Tribenzylphosphine (PBz_3) Complexes of Copper(I): Solid State ^{31}P NMR Studies and the Crystal Structure of $[Cu(PBz_3)_2]PF_6$. Ainscough, E. W.; Brodie, A. M.; Burrell, A. K.; Hanna, J. V.; Healy, P. C.; Waters, J. M. *Inorg. Chem.* (1999) 38, 201-203.

14. Phenylcyanamidocopper(I) and silver(I) complexes: synthetic and structural studies. Ainscough, E. W.; Brodie, A. M.; Cresswell, R. J.; Turnbull, J. C.; Waters, J. M. *Croatica Chem. Acta* (1999) in the press (invited paper).

15. H···Br hydrogen bonding in *trans*-tetraaquabis(*N*-acetonitrile)cobalt(II) bromide. Depree, C. V.; Ainscough, E. W.; Brodie, A. M.; Gainsford, G. J.; Lensink, C. *Acta Crystallogr. Section C* (1999) in the press.

16. Polymer building blocks: a $CuCl_2$-bridged phosphazene dimer containing κ^5N coordinated Cu(II). Ainscough, E. W.; Brodie, A. M.; Depree, C. V. *J. Chem. Soc., Dalton Trans.* accepted for publication.

CHAPTER 4

MISCELLANEOUS ORGANOMETALLIC COMPOUNDS

CHAPTER 4

1. Preparation and reactivity of some cationic rhenium carbonyl complexes. Brodie, A. M.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Organometal. Chem.* (1970) 24, 201-3.

2. π-Hetero-1,3-diene complexes of iron carbonyl. Brodie, A. M.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *J. Chem. Soc., Dalton Trans.* (1972) 2031-5.

3. Tricarbonyl(polyene aldehyde)iron complexes. Brodie, A. M.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* (1973) 1997-2002.

4. The synthesis of a ferrocenyl Schiff base pyridine borane complex using $NaBH_4$. Ainscough, E. W.; Brodie, A. M.; Lowe, A. D.; Waters, J. M. *Inorg. Chim. Acta* accepted for publication.